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Application of the QCM in lead acid batteries electrolyte measurements

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Abstract

This paper describes the application of a Quartz Crystal Microbalance (QCM) sensor in density-viscosity measurements of the electrolyte of the lead acid batteries. In battery applications, especially in automotive applications, submarines and remote communication systems it is necessary to know the state of charge of the batteries in order to manage them efficiently [1]. One of the physical parameters with information about the state of charge is the electrolyte density; the product $\eta\rho^{1/2}$ as well varies with the state of charge [2]. Due the quartz crystal oscillator frequency depends on the density and the viscosity (1), it is possible to measure the electrolyte density changes by means of a QCM sensor. The frequency shift is monitoring in solutions with H_2SO_4 concentration in the battery electrolyte range. Furthermore, real time experiments are conducted, placing the quartz crystal inside the battery cell.

Keywords: Quartz cristal microbalance, battery electrolyte, density, viscosity.

1. Introduction

Quartz crystal oscillators are piezoelectric devices which are used in electronic circuitry for a variety of purposes, because they can provide a highly accurate timing signal based upon their frequency of oscillation. If a mass is adsorbed or placed onto the quartz crystal surface, the frequency of oscillation changes in proportion to the amount of mass. Therefore, these devices can be used as high sensitivity microbalances intended to measure mass changes in the nanogram range by coating the crystal with a material which is selective towards the species of interest [3]. On the other hand, when the QCM sensor is in contact with a Newtonian liquid, the frequency shift, Δf, depends on the density, ρ, and the viscosity, η, of the liquid, according with Kanazawa and Gordon's equation [4]:

$$\Delta f = -\frac{2.26x10^{-6} f^{3/2}\sqrt{\eta\rho}}{\sqrt{4\pi}} \qquad (1)$$

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Where f is the quartz crystal fundamental frequency. In this way, these devices also can be used as sensors for simultaneous measurement of density and viscosity of liquids.

During the charge and discharge process in lead acid batteries, since H_2SO_4 participates in the electrode reaction, the electrolyte becomes more diluted during discharge and is re-concentrated during charge [2]. In this sense, some parameters vary according to the acid concentration present in the electrolyte (table 1). Furthermore, the acid dilution provides a tool to determine the state of charge with the aid of density measurements. The product $\eta\rho^{1/2}$ as well varies with the state of charge (figure 1).

When QCM sensor is in contact with the electrolyte, there is a frequency shift, Δf, which depends on the density, ρ, and the viscosity, η, of the electrolyte like in (1). Then, it is possible to measure electrolyte density-viscosity changes by means of the measurement of the frequency drift of a QCM sensor.

Table 1. Electrolyte parameters for different states of charge

% Acid	Relative density	Concentration (gl^1)	Concentration (mol l^-1)	Index of Refraction	Relative viscosity
8	1.0541	84.2	0.858	1.3427	1.180
10	1.0680	106.6	1.087	1.3451	1.228
12	1.0821	129.6	1.322	1.3475	1.279
14	1.0966	153.3	1.563	1.3500	1.334
16	1.1114	177.5	1.810	1.3525	1.396
18	1.1265	202.4	2.064	1.3550	1.467
20	1.1418	228.0	2.324	1.3576	1.543
22	1.1575	254.2	2.592	1.3602	1.621
24	1.1735	281.1	2.866	1.3628	1.703
26	1.1893	308.7	3.147	1.3653	1.793
28	1.2052	336.9	3.435	1.3677	1.890
30	1.2213	365.7	3.729	1.3701	1.997
32	1.2353	395.3	4.030	1.3725	2.118
34	1.2518	425.6	4.339	1.3749	2.250
36	1.2685	456.7	4.656	1.3773	2.387
38	1.2855	488.5	4.981	1.3797	2.528
40	1.3028	521.1	5.313	1.3821	2.685

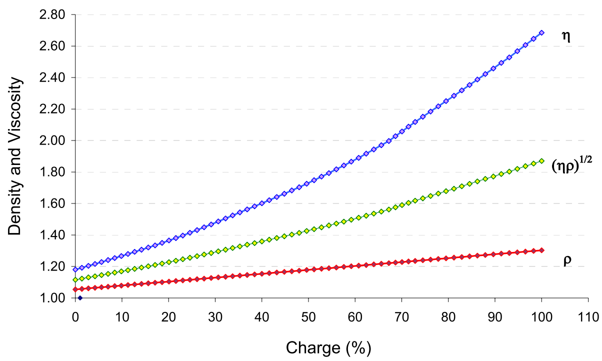


Fig. 1. Density, viscosity and product $\eta\rho^{1/2}$ dependence with battery state of charge

2. Calibration of the QCM sensor in H_2SO_4 solutions

A 9MHz Miller oscillator with stable temperature is tested in lead acid battery electrolyte (sulphuric acid diluted). The quartz crystal is immersed in sulphuric acid solution (H_2SO_4 + H_2O) with a concentration of 23%, the liquid temperature is stabilized at 31ºC. The solution concentration has a density of 1.1655 g/cc at a room temperature. The oscillator frequency is monitoring as well as the liquid temperature. Periodically, a little quantities of concentrated H_2SO_4 (95%) are added in order to increase the liquid density and simulate real conditions during the battery charge process. Figure 2.a shows the frequency changes when concentrated acid is added as soon as the liquid temperature. Frequency has some peaks at its high value; it corresponds with pure acid addition. This addition produce an exothermic reaction and frequency is affected by temperature increment, some time later (a few minutes) liquid temperature returns to its stable value (31ºC) and frequency responds only to the parameter $\eta\rho^{1/2}$. The procedure is repeated for seven times until density value 1.3028 g/cc.

In Figure 2.b it can be seen the calibration plot; the experimental sensitivity obtained is calculated according (2):

$$k_{\exp erimental} = \frac{\Delta f}{\Delta\sqrt{\eta\rho}} = -2.2\frac{kHz}{\sqrt{\frac{g}{cm^3}cp}} \qquad (2)$$

The theoretical sensitivity coefficient calculated by (1) is $k_{theoretical}$= -1.7 kHz /(cp.g/cm^3)$^{1/2}$. It can be noted that the predicted coefficient by Kanazawa & Gordon (1) and the experimental coefficient (2) are very close as expected

The study of the short term stability is carried out [5]; Allan deviations are calculated for each pair $\eta\rho^{1/2}$. The greatest value of the Allan deviation (1.1 x10^{-7} Hz) represents the worst case. In this situation, the experimental quality factor, Q_{exp}, is 1253 and a resolution of 6x10^{-4} (cp·g/cm^3)$^{1/2}$ can be achieved. With this resolution, changes in the SOC of the battery of about 0.1 % can be detected, for temporal measurements with 1s< t <10s.

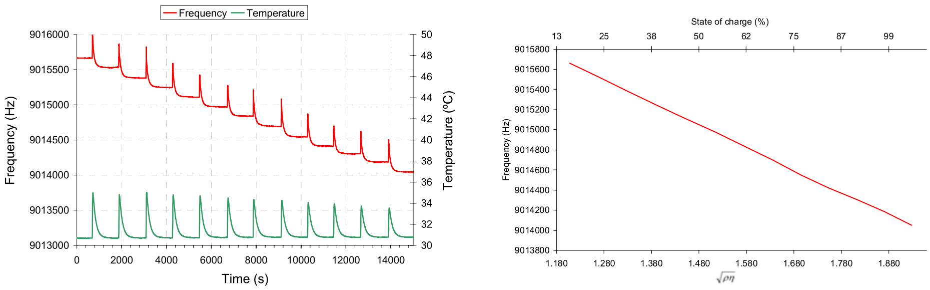


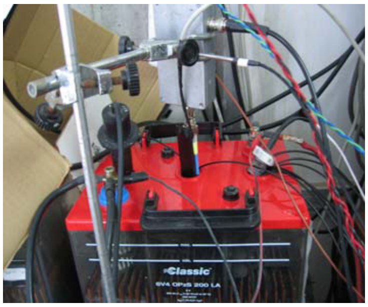
Fig. 2. (a) QCM sensor frequency and liquid temperature during solutions test; (b) Calibration plot of the QCM sensor

3. QCM behavior in electrolyte measurements during a battery charge

After checking the behavior of the QCM in solutions, the sensor is tested during a charging process. In real time application, it is not possible to control the temperature of the electrolyte, for this reason, an evaluation of QCM thermal behavior of the QCM in liquid media (electrolyte) is conducted [6][7]. Equation 2 gives the adequate temperature compensation in order to have a frequency referenced to T_0 (25 degrees Celsius).

$$f_{corrected} = f_{liquid} - 75.24\,(T-T_0) - 1.2209\,(T-T_0)^2 - 0.1222\,(T-T_0)^3 \qquad (2)$$

The sensor is placed inside the battery cell (figure 3.a) in the top zone of the battery. Figure 3.b shows the frequency monitoring during the charge. The sensor tendency is according the expected: in the top zone, and due the electrolyte stratification, the parameters density and viscosity don't increase their values until the charge is advanced and bubbling occurs [2].



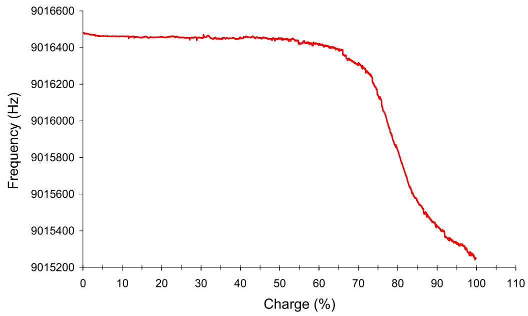


Fig. 3. (a) Photograph of the QCM sensor placed inside the battery; (b) QCM sensor during a real time battery charge

4. Conclusions

A QCM sensor with 9 MHz Miller oscillator is tested in sulphuric acid solutions in order to know its behavior. The frequency varies according to the change in the solutions density and it has a lineal relation with the product $\eta\rho^{1/2}$. Thermal test is conducted and temperature compensation coefficients in liquid medium (electrolyte) were obtained prior to check QCM in real time battery charge. The sensor frequency response was according the expected evolution of the viscosity-density parameters during the real charging process.

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